

THE CLASSIFICATION OF THE SPECTRUM OF Pb II

By

LESTER THOMAS EARLS

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
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The Classification of the First Spark Spectrum of Lead: Pb II

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The spectrum of Pb II as excited in a Schüler hollow cathode discharge in helium has been photographed in the region from 800A to 10,000A. With these data the classification given by Fraülein H. Gieseler (*Zeits. f. Physik* **42**, 265 (1927)) has been corrected and extended. 247 lines have been classified, which locate 89 levels below the ionization level of the ion. These include the *s*, *p*, *d*, *f* and *g* series based on $6s^2$, extending to values of *n* of from 14 to 19, and all levels of the other configurations which are

expected below ionization. The assignment of these levels is checked by series considerations, by Zeeman effect data, by hyperfine structure data, by comparison with the similar spectra Ge II and Sn II, and by the agreement with the regular and irregular doublet laws in the isoelectronic sequence with Tl I and Bi III. The observed anomalous location of a number of the levels is shown to be explained qualitatively by the perturbations expected between the even levels.

MEASUREMENTS of the lead spectrum have been obtained by various experimenters, notably Eder and Valenta,¹ Exner and Haschek,² Thalén,³ and Klein⁴ in the visible and ultraviolet, Randall⁵ in the infrared, and Carroll,⁶ Lang,⁷ and Arvidsson⁸ in the vacuum region. The sources used in these investigations included arc in air and vacuum, spark in air and vacuum, and electrodeless discharge. The only important work on the classification of the Pb II spectrum was done by Fraülein H. Gieseler.⁹ She photographed the ultraviolet and visible region of the emission from a Schüler hollow cathode tube and supplemented these data with vacuum region measurements by various workers. 72 lines were used to establish 36 levels, several of which appear to be erroneous in the light of the present investigation.

Theory predicts the level $6s^2 6p\ ^2P_{1/2}$ as the lowest state of singly ionized lead. Predicted excited states include the several series *ms*, *mp*, *md*, *mf*, ... when both *6s* electrons remain unexcited; and, when one of these is raised to an excited state, configurations of the types $6s6p^2$, $6s6p6d$, $6s6d^2$, etc. By a consideration of the energy values in Pb III¹¹ corresponding to the excitation of a *6s* electron to *6p*, *6d*, etc., states, it becomes apparent that the levels from $6s6p6d$,

$6s6d^2$, etc., lie considerably above the ionization potential of Pb II. The same is true of the possible configurations $6s6p7s$, etc., on the basis of a Ritzian formula calculation. This leaves only the $6s^2 mx$ series and the $6s6p^2$ levels to be expected below ionization. The $6s6p^2$ configuration gives rise to the eight levels $^4P_{1, 1\frac{1}{2}, 2\frac{1}{2}}$, $^2D_{3\frac{1}{2}, 2\frac{1}{2}}$, $^2P_{1, 1\frac{1}{2}}$, and 2S_1 in Russell-Saunders notation, and of course to an equal number of levels in any coupling.

EXPERIMENTAL

The excitation produced in a Schüler hollow cathode discharge in a rare gas atmosphere tends to be limited by the energy of the reactions between metal ions and metastable rare gas atoms, or between metal atoms and rare gas ions.¹⁰ Since the ionization energy of Pb I is about 60,000 cm⁻¹ and that of Pb II about 120,000 cm⁻¹, it is evident that a discharge in helium (metastable state 160,000 cm⁻¹; ionization energy 198,000 cm⁻¹) should excite all levels of Pb II, but none of Pb III. Hence this arrangement was chosen as a source in the present investigation. Two mercury vapor pumps in series circulated helium through the discharge tube and suitable liquid air and charcoal traps. A high voltage direct-current generator served as a source of potential (700 to 1000 volts), but the ballast resistance in series with the discharge decreased considerably the effective voltage at the terminals of the tube. The current used was approximately 125 m.a. Cathodes of molybdenum and of iron

¹ Eder and Valenta, *Wellenlängenmessungen*, Wien, Ber. **119**, 519 (1910).

² Exner and Haschek, *Wellenlängentabellen*, Leipzig, 1904.

³ Thalén, *Nova acta reg. soc. sc. Upsal.* **3**, 6 (1868).

⁴ Klein, *Zeits. f. Wiss. Phot.* **12**, 16 (1913).

⁵ Randall, *Astrophys. J.* **34**, 1 (1911).

⁶ Carroll, *Trans. Roy. Soc. A* **225**, 357 (1925).

⁷ Lang, *Trans. Roy. Soc. A* **224**, 371 (1924).

⁸ Arvidsson, *Ann. d. Physik* **12**, 787 (1932).

⁹ Gieseler, *Zeits. f. Physik* **42**, 265 (1927).

¹⁰ Sawyer, *Phys. Rev.* **36**, 44 (1930).

were used at different times. In each case a few of the strongest lines due to the cathode material showed in the emission. The lead (chemically pure) was laid within the cylindrical cathode in small pieces which promptly melted in the heat of the discharge. Photographs were taken under two conditions of discharge. In the first the discharge was started in the normal helium pressure. The inflow of helium was then almost completely shut off, and within a few seconds the pumps removed the helium to a point at which the discharge changed from a yellowish appearance to a deep blue. Under these conditions it appeared that the discharge was carried primarily by the lead vapor; the helium lines remained, but were considerably weakened. This method of operation gave a number of lines which are classified by Smith¹¹ as Pb III and Pb IV. The second condition of discharge involved the continued circulation of the helium throughout the time of the photograph; in this case the lines due to higher ionization were much weaker or entirely absent.

The spectrum was photographed from 800A to 10,000A. From 800A to 2400A a normal incidence concave grating vacuum spectrograph was used. This instrument¹² (1 m radius, 14,400 lines per inch) had a dispersion of about 17A/mm. Between 2100A and 5500A two Hilger quartz instruments were used (types E-1 and E-3), and from 5100A to 10,000A a spectrograph of design similar to the E-1, with glass optical system, was utilized. In the vacuum photographs He, Hg and H lines appeared as impurity lines and were used as standards. Iron arc comparison spectra were applied to all other photographs except those in the infrared, where a neon tube was used. In addition, plates from the first order of a 21-foot concave grating, covering the region 2200A to 10,000A, were kindly loaned by Dr. J. L. Rose, of New York University. The excitation for these photographs was also a hollow cathode discharge in helium. All plates were measured on a Gaertner comparator. The calculated wavelengths in air were reduced to wave numbers by means of Kayser's table. For wavelengths greater than 2100A the wave number values are probably correct to about one wave per centimeter; for

shorter wavelengths the error may be as high as 10 or 15 cm⁻¹, especially for weak lines.

DATA AND CLASSIFICATION

The above experimental work provided 340 lines in the vacuum region (ν 185,000 to ν 47,000) and about 730 lines in the region from ν 47,000 to ν 10,000. About 60 of the strongest of these lines have been classified by Gieseler and Grotrian¹³ in Pb I, and a smaller number by Smith¹¹ and others in Pb III or Pb IV. The 247 lines now classified in Pb II are listed in Table I. Fourteen of these lines, lying in the vacuum region, were also observed by Arvidsson.⁸ His measurements, which are more accurate than is claimed for the vacuum data of the present work, are included in Table I and used for the location of the $6p^2P$ levels. The classified lines determine 89 levels; these are tabulated in Table II, with their effective quantum numbers in the case of series members. It will be noted that the effective quantum numbers of the two odd series $6s^2mp^2P$ and $6s^2mf^2F$ are very regular as they approach a limiting value for large m , though all 2F members are inverted. The even series $6s^2mg^2G$ is also regular; its doublets are unresolved. The other two even series $6s^2ms^2S$ and $6s^2md^2D$ show pronounced irregularities in the lower members; these irregularities are explained below in terms of perturbations from the intermingling levels from the $6s6p^2$ configuration.

In determining the ionization potential of Pb II, use has been made of the series limits of the 2F and 2G series; these limits are located to within less than 1 cm⁻¹. Thus the value of the ionization potential (121,243 cm⁻¹) is determined within the error involved in the vacuum data on transitions to the lowest term $6s^26p^2P_1$. By using Arvidsson's data⁸ for these lines (for which his estimate of probable error is 2 or 3 cm⁻¹), the ionization potential is correct to 2 or 3 cm⁻¹. The location of the next series, $6s^2mh^2H$, could be predicted very closely, but transitions from the low members were out of experimental range, and those from the higher members were not observed.

Comparison of the Pb II spectrum with the similar spectra of Ge II¹⁴ and Sn II¹⁴ has been

¹¹ Smith, Phys. Rev. **34**, 393 (1926); **36**, 1 (1930).

¹² Sawyer, J. O. S. A. **15**, 307 (1927).

¹³ Gieseler and Grotrian, Zeits. f. Physik **39**, 377 (1926).

¹⁴ Bacher and Goudsmit, Atomic Energy States (1932).

TABLE I. Classified lines in Pb II.

Classification	$\lambda(A)$	$\nu(\text{cm}^{-1})$	Intensity	$\Delta\nu$	Notes	Classification	$\lambda(A)$	$\nu(\text{cm}^{-1})$	Intensity	$\Delta\nu$	Notes
$7D_{1\frac{1}{2}} - 9P_{\frac{1}{2}}$	9864.2	10139	00	-1		$p^2 2D_{\frac{3}{2}} - 10P_{\frac{1}{2}}$	4788.1	20879	6	0	h_6
$5G - 9F_{\frac{3}{2}}$	9440.1	10593	1	-2		$p^2 2D_{1\frac{1}{2}} - 9P_{\frac{1}{2}}$	4684.9	21339	5	0	h_7
$5F_{\frac{3}{2}} - 5G$	9063.7	11030	10	0	$x h_0$	$7D_{1\frac{1}{2}} - 10F_{\frac{3}{2}}$	4677.8	21372	7	1	
$5F_{\frac{3}{2}} - 5G$	9050.7	11045	10	0	$x h_0$	$8P_{\frac{1}{2}} - 14D_{1\frac{1}{2}}$	4668.9	21412	0	0	
$8D_{\frac{3}{2}} - 10F_{\frac{3}{2}}$	8723.1	11461	3	2		$7D_{\frac{3}{2}} - 11F_{\frac{3}{2}}$	4666.5	21423	1	1	
$9P_{\frac{1}{2}} - 12D_{1\frac{1}{2}}$	8721.3	11463	0	0		$8P_{\frac{1}{2}} - 14D_{\frac{3}{2}}$	4665.5	21428	5	0	h_0
$6F_{\frac{3}{2}} - 8G$	8719.7	11465	5	0	h_0	$5F_{\frac{3}{2}} - 8G$	4582.3	21817	10	0	$x h_0$
$6F_{\frac{3}{2}} - 8G$	8710.1	11478	7	0	h_0	$8P_{\frac{1}{2}} - 13D_{1\frac{1}{2}}$	4581.3	21822	4	0	h_0
$8P_{\frac{1}{2}} - 10S_{\frac{1}{2}}$	8550.6	11692	2	0		$5F_{\frac{3}{2}} - 8G$	4579.1	21832	10	0	$x h_0$
$7P_{1\frac{1}{2}} - p^2 2D_{\frac{3}{2}}$	8545.0	11699	7	1	h_6	$p^2 2D_{1\frac{1}{2}} - 9P_{1\frac{1}{2}}$	4557.2	21937	2	0	h_7
$7P_{1\frac{1}{2}} - 8S_{\frac{1}{2}}$	8395.6	11908	10	0	h_{12}	$8P_{1\frac{1}{2}} - 15D_{\frac{3}{2}}$	4544.8	21997	4	0	h_0
$p^2 2D_{1\frac{1}{2}} - 8P_{\frac{1}{2}}$	8335.0	11994	6	1	h_7	$7D_{\frac{3}{2}} - 12F_{\frac{3}{2}}$	4499.6	22218	0	-2	
$8D_{1\frac{1}{2}} - 10F_{\frac{3}{2}}$	8152.0	12263	0	0		$p^2 4P_{\frac{3}{2}} - 8P_{1\frac{1}{2}}$	4476.3	22334	3	-1	h_{11}
$9P_{\frac{1}{2}} - 13D_{1\frac{1}{2}}$	8013.0	12476	00	1		$8P_{1\frac{1}{2}} - 16D_{\frac{3}{2}}$	4454.9	22441	1	0	h_0
$8D_{\frac{3}{2}} - 11F_{\frac{3}{2}}$	7973.2	12538	00	0		$7D_{1\frac{1}{2}} - 11F_{\frac{3}{2}}$	4453.8	22446	3	0	
$9P_{1\frac{1}{2}} - 14D_{\frac{3}{2}}$	7906.8	12644	0	2		$8P_{\frac{1}{2}} - 14D_{1\frac{1}{2}}$	4428.7	22574	2	-1	h_0
$8P_{\frac{1}{2}} - 10S_{\frac{1}{2}}$	7777.8	12853	2	0		$6D_{1\frac{1}{2}} - 5F_{\frac{3}{2}}$	4386.4	22791	20	-2	$x h_4 Z$
$6F_{\frac{3}{2}} - 9G$	7739.8	12916	2	0	h_0	$8P_{1\frac{1}{2}} - 17D_{\frac{3}{2}}$	4386.0	22793	2	0	
$6F_{\frac{3}{2}} - 9G$	7732.3	12930	4	-1	h_0	$p^2 2D_{\frac{3}{2}} - 8F_{\frac{3}{2}}$	4352.7	22968	10	0	h_6
$8P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$	7679.4	13018	1	1		$p^2 2D_{\frac{3}{2}} - 8F_{\frac{3}{2}}$	4351.5	22974	3	0	
$6F_{\frac{3}{2}} - 12D_{\frac{3}{2}}$	7664.8	13043	0	1		$8P_{1\frac{1}{2}} - 18D_{\frac{3}{2}}$	4332.2	23077	0	0	
$8P_{1\frac{1}{2}} - 9D_{\frac{3}{2}}$	7632.2	13098	10	0	h_0	$8P_{\frac{1}{2}} - 15D_{1\frac{1}{2}}$	4319.2	23146	1	0	h_0
$7D_{\frac{3}{2}} - 7F_{\frac{3}{2}}$	7558.7	13226	10	-1	h_{13}	$7D_{1\frac{1}{2}} - 12F_{\frac{3}{2}}$	4302.1	23238	1	0	
$7D_{\frac{3}{2}} - 7F_{\frac{3}{2}}$	7553.7	13234	1	0		$5F_{\frac{3}{2}} - 9G$	4296.6	23268	6	0	$x h_0$
$8D_{\frac{3}{2}} - 12F_{\frac{3}{2}}$	7499.6	13330	00	0		$5F_{\frac{3}{2}} - 9G$	4293.8	23283	7	0	$x h_0$
$p^2 2D_{\frac{3}{2}} - 6F_{\frac{3}{2}}$	7193.6	13897	20	-1	h_6	$8P_{1\frac{1}{2}} - 19D_{\frac{3}{2}}$	4288.9	23310	00	0	
$p^2 2D_{\frac{3}{2}} - 6F_{\frac{3}{2}}$	7187.1	13910	2	-1		$8S_{\frac{1}{2}} - 11P_{\frac{1}{2}}$	4272.5	23399	3	-1	(g)
$6F_{\frac{3}{2}} - 10G$	7165.1	13953	2	-1	h_0	$6D_{\frac{3}{2}} - 5F_{\frac{3}{2}}$	4245.1	23550	20	0	$x h_2 Z$
$6F_{\frac{3}{2}} - 10G$	7158.7	13965	2	0	h_0	$6D_{\frac{3}{2}} - 5F_{\frac{3}{2}}$	4242.5	23565	9	0	$x h_2 Z$
$6F_{\frac{3}{2}} - 13D_{\frac{3}{2}}$	7114.7	14051	0	1		$8P_{\frac{1}{2}} - 16D_{1\frac{1}{2}}$	4237.6	23591	0	0	h_0
$8P_{\frac{1}{2}} - 9D_{1\frac{1}{2}}$	7050.7	14179	9	1	h_0	$8S_{\frac{1}{2}} - 11P_{1\frac{1}{2}}$	4232.4	23620	2	0	
$7D_{1\frac{1}{2}} - 7F_{\frac{3}{2}}$	7013.2	14255	10	-1	$xxx h_0$	$p^2 2D_{\frac{3}{2}} - 11P_{1\frac{1}{2}}$	4195.5	23828	3	0	h_6
$7D_{\frac{3}{2}} - 10P_{1\frac{1}{2}}$	6872.0	14548	0	-1		$7D_{1\frac{1}{2}} - 13F_{\frac{3}{2}}$	4193.7	23838	00	0	
$6F_{\frac{3}{2}} - 11G$	6791.7	14720	2	-1	h_0	$8P_{1\frac{1}{2}} - 17D_{1\frac{1}{2}}$	4175.0	23945	00	0	
$7P_{\frac{1}{2}} - 8S_{\frac{1}{2}}$	6790.8	14722	10	-1	h_{12}	$7P_{1\frac{1}{2}} - 9S_{\frac{1}{2}}$	4152.8	24073	10	1	$x h_3 Z$
$6F_{\frac{3}{2}} - 11G$	6785.9	14732	3	0	h_0	4113.4	24304	4	0	$x h_0$	
$7S_{\frac{1}{2}} - 7P_{\frac{1}{2}}$	6660.0	15011	50	0	$x h_8 Z$	$5F_{\frac{3}{2}} - 10G$	4110.8	24319	5	0	$x h_0$
$7D_{1\frac{1}{2}} - 10P_{\frac{1}{2}}$	6569.4	15218	5	-2		3987.6	25070	2	1	$x h_0$	
$8S_{\frac{1}{2}} - 9P_{\frac{1}{2}}$	6558.7	15243	3	-1		$5F_{\frac{3}{2}} - 11G$	3985.2	25086	2	0	$x h_0$
$6F_{\frac{3}{2}} - 12G$	6533.1	15302	4	0	h_0	$p^2 2D_{\frac{3}{2}} - 9F_{\frac{3}{2}}$	3971.3	25174	4	-1	h_6
$6F_{\frac{3}{2}} - 12G$	6527.8	15315	5	0	h_0	$p^2 2D_{1\frac{1}{2}} - 7F_{\frac{3}{2}}$	3927.3	25456	6	-1	h_7
$8P_{1\frac{1}{2}} - 11S_{\frac{1}{2}}$	6518.2	15337	8	-1	h_0	$5F_{\frac{3}{2}} - 12G$	3896.9	25654	0	0	
$7D_{1\frac{1}{2}} - 10P_{1\frac{1}{2}}$	6422.9	15565	0	2		$5F_{\frac{3}{2}} - 12G$	3894.6	25669	1	0	
$6F_{\frac{3}{2}} - 13G$	6345.0	15756	5	0	h_0	$p^2 2D_{\frac{3}{2}} - 12P_{1\frac{1}{2}}$	3880.5	25763	0	0	
$6F_{\frac{3}{2}} - 13G$	6339.8	15769	3	0	h_0	$5F_{\frac{3}{2}} - 13G$	3829.2	26108	0	0	
$8S_{\frac{1}{2}} - 9P_{1\frac{1}{2}}$	6311.5	15840	9	0		$7P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	3827.2	26121	3	1	$h_{10} Z$
$p^2 2D_{\frac{3}{2}} - 9P_{1\frac{1}{2}}$	6229.7	16048	10	0	h_6	$p^2 4P_{1\frac{1}{2}} - 5F_{\frac{3}{2}}$	3785.9	26406	10	-1	$xx h_3 Z$
$6F_{\frac{3}{2}} - 14G$	6203.7	16115	1d	0	h_0	$p^2 2D_{1\frac{1}{2}} - 10P_{\frac{1}{2}}$	3784.0	26419	2	-2	
$6F_{\frac{3}{2}} - 14G$	6198.8	16128	1d	0	h_0	$6D_{1\frac{1}{2}} - 8P_{1\frac{1}{2}}$	3772.9	26497	00	1	
$8P_{1\frac{1}{2}} - 10D_{1\frac{1}{2}}$	6181.9	16172	7	-1	$h_0 (a)$	$p^2 2D_{\frac{3}{2}} - 10F_{\frac{3}{2}}$	3746.9	26681	4	0	h_6
$8P_{1\frac{1}{2}} - 10D_{\frac{3}{2}}$	6160.0	16229	10	0	h_0	$p^2 2D_{1\frac{1}{2}} - 10P_{1\frac{1}{2}}$	3734.8	26767	2	1	
$6F_{\frac{3}{2}} - 15G$	6094.0	16405	0d	0	h_0	$7P_{1\frac{1}{2}} - 8D_{\frac{3}{2}}$	3718.2	26887	7	0	$x h_3 Z$
$6F_{\frac{3}{2}} - 15G$	6089.4	16418	1	0	h_0	$7P_{1\frac{1}{2}} - 8D_{2\frac{1}{2}}$	3714.0	26918	10	0	$h_0 Z$
$5F_{\frac{3}{2}} - 6G$	6081.5	16439	40	0	$x h_0$	$7P_{1\frac{1}{2}} - p^2 2S_{\frac{1}{2}}$	3699.2	27025	2	0	h_{21}
$5F_{\frac{3}{2}} - 6G$	6075.8	16454	40	0	$x h_0$	$p^2 2D_{\frac{3}{2}} - 13P_{1\frac{1}{2}}$	3689.0	27100	0	0	(i)
$8P_{\frac{1}{2}} - 11S_{\frac{1}{2}}$	6041.4	16548	8d	0	h_7	$6D_{\frac{3}{2}} - 8P_{1\frac{1}{2}}$	3665.6	27273	4	1	h_2
$p^2 4P_{\frac{3}{2}} - 7P_{\frac{1}{2}}$	6009.7	16635	9	1	h_{13}	$7P_{1\frac{1}{2}} - p^2 2P_{1\frac{1}{2}}$	3649.0	27397	3	0	h_{11}
$7D_{\frac{3}{2}} - 8F_{\frac{3}{2}}$	6007.5	16641	2	1		$p^2 2D_{\frac{3}{2}} - 11F_{\frac{3}{2}}$	3601.8	27756	3	0	h_6
$7P_{1\frac{1}{2}} - 7D_{1\frac{1}{2}}$	5876.7	17011	10	1	$xxx h_0 Z (c)$	$p^2 2D_{\frac{3}{2}} - 12F_{\frac{3}{2}}$	3501.9	28548	2	0	h_6
$8P_{\frac{1}{2}} - 10D_{1\frac{1}{2}}$	5767.9	17333	10	-1	h_0	$p^2 2D_{1\frac{1}{2}} - 8F_{\frac{3}{2}}$	3463.6	28863	6	0	h_7
$7D_{\frac{3}{2}} - 11P_{1\frac{1}{2}}$	5713.8	17496	4	0		$7P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	3455.0	28935	8	0	$h_{10} Z$
$7D_{1\frac{1}{2}} - 8F_{\frac{3}{2}}$	5660.1	17663	2	-1		$p^2 4P_{1\frac{1}{2}} - 8P_{\frac{1}{2}}$	3453.0	28952	0	1	
$7S_{\frac{1}{2}} - 7P_{1\frac{1}{2}}$	5608.8	17824	10	0	$x h_8 Z$	$p^2 4P_{\frac{3}{2}} - 6F_{\frac{3}{2}}$	3451.7	28963	9	0	$xx h_1 Z$
$7P_{1\frac{1}{2}} - 7D_{\frac{3}{2}}$	5544.6	18031	10	1	$h_{14} Z (d)$	$p^2 4P_{\frac{3}{2}} - 6F_{\frac{3}{2}}$	3450.0	28976	2	0	$xx h_1$
$8P_{1\frac{1}{2}} - 11D_{1\frac{1}{2}}$	5483 ?	18230?	000			$p^2 2D_{\frac{3}{2}} - 13F_{\frac{3}{2}}$	3429.6	29149	1	0	
$8P_{1\frac{1}{2}} - 11D_{\frac{3}{2}}$	5472.4	18268	7	1	$xxx h_0$	$p^2 2D_{1\frac{1}{2}} - 11P_{\frac{1}{2}}$	3389.4	29495	2	0	h_7
$p^2 4P_{\frac{3}{2}} - 5F_{\frac{3}{2}}$	5372.1	18608	10	1	$xx h_1 Z$	$p^2 2D_{\frac{3}{2}} - 14F_{\frac{3}{2}}$	3375.6	29616	00	0	
$p^2 4P_{\frac{3}{2}} - 5F_{\frac{3}{2}}$	5367.3	18624	10	0	$xx h_1$	$7P_{1\frac{1}{2}} - p^2 2S_{\frac{1}{2}}$	3350.5	29838	00	0	
$8P_{\frac{1}{2}} - 12S_{\frac{1}{2}}$	5308.2	18834	3	1	h_0	$7P_{1\frac{1}{2}} - p^2 2P_{1\frac{1}{2}}$	3309.2	30210	6	0	h_{11}
$7D_{\frac{3}{2}} - 9F_{\frac{3}{2}}$	5306.8	18839	6	2	h_{13}	$7P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	3261.0	30656	6	2	h_0
$8P_{1\frac{1}{2}} - 13S_{\frac{1}{2}}$	5191.4	19257	1	1		$p^2 2D_{1\frac{1}{2}} - 9F_{\frac{3}{2}}$	3217.9	31067	3	0	h_7
$p^2 4P_{\frac{3}{2}} - 7P_{1\frac{1}{2}}$	5163.8	19360	7	1	$h_7' (e)$	$p^2 4P_{\frac{3}{2}} - 9P_{1\frac{1}{2}}$	3213.0	31114	00	1	
$p^2 2D_{\frac{3}{2}} - 11D_{1\frac{1}{2}}$	5155.8	19390	7	-1	h_0	$p^2 2D_{1\frac{1}{2}} - 12P_{1\frac{1}{2}}$	3173.5	31502	0	0	
$p^2 2D_{\frac{3}{2}} - 7F_{\frac{3}{2}}$	5111.9	19557	10	0	h_6	$7P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$	3125.6	31985	6	0	h_0
$p^2 2D_{\frac{3}{2}} - 7F_{\frac{3}{2}}$	5109.6	19566	3	0	h_6	$7P_{1\frac{1}{2}} - 9D_{2\frac{1}{2}}$	3117.7	32064	10	0	h_0
$8P_{1\frac{1}{2}} - 12D_{1\frac{1}{2}}$	5081.2	19647 (calc.)	3	-1	h_0	$p^2 2D_{1\frac{1}{2}} - 10F_{\frac{3}{2}}$	3068.5?	32574?	2		$h_7 (j)$
$8P_{1\frac{1}{2}} - 12D_{\frac{3}{2}}$	5074.6	19700	10	1	$x h_0$	$p^2 2D_{1\frac{1}{2}} - 13P_{1\frac{1}{2}}$	3039.9	32886	00	-2	
$5F_{\frac{3}{2}} - 7G$	5070.7	19716	10	0	$x h_0$	$6D_{1\frac{1}{2}} - 6F_{\frac{3}{2}}$	3016.4	33142	10	-1	$x h_4 Z$
$5F_{\frac{3}{2}} - 7G$	5049.3	19799	9	-1	h_7	$7P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	2986.9	33470	4	1	h_0
$p^2 2D_{1\frac{1}{2}} - 6F_{\frac{3}{2}}$	5042.5	19825	50	0	$xxx h_0 Z$	$p^2 2D_{$					

TABLE I.—Continued.

Classification	$\lambda(A)$	$\nu(\text{cm}^{-1})$	Intensity	$\Delta\nu$	Notes	Classification	Wave-length (A_{vac})	Wave No. (cm^{-1})	Intensity	$\Delta\nu$	Notes	ν Arvid.	In- ten. Arv.	$\Delta\nu$ Arv.
$6P_{1\frac{1}{2}} - 6F_{3\frac{1}{2}}$	2719.8	36758	4	-1	$xx\ h_3\ Z$	$6P_{1\frac{1}{2}} - 6P_{1\frac{1}{2}}$	1203.63	83082	10	1		83083	4	0
$7S_{\frac{1}{2}} - 8P_{1\frac{1}{2}}$	2717.5	36789	4	1	$h_{20}\ Z$	$6P_{1\frac{1}{2}} - 9S_{\frac{1}{2}}$	1145.91	87267	4	-2				
$7P_{\frac{1}{2}} - 11S_{\frac{1}{2}}$	2693.6	37114	0	1		$6P_{1\frac{1}{2}} - 9S_{\frac{1}{2}}$	1133.14	88250	10	-2		88248	7	0
$7P_{\frac{1}{2}} - 11D_{3\frac{1}{2}}$	2684.9	37235	2	0	h_0	$6P_{1\frac{1}{2}} - 8S_{\frac{1}{2}}$	1121.36	89177	10	3		89180	0	0
$7P_{\frac{1}{2}} - 10D_{1\frac{1}{2}}$	2634.3	37950	4	0	h_0	$6P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	1119.57	89320	10	-7		89314	4d	-1
$6P_{1\frac{1}{2}} - 8F_{3\frac{1}{2}}$	2628.3	38036	3	-1		$6P_{1\frac{1}{2}} - 8D_{3\frac{1}{2}}$	1109.84	90103	10	6		90110	1	-1
$6P_{1\frac{1}{2}} - 8F_{1\frac{1}{2}}$	2608.4	38326	2	1		$6P_{1\frac{1}{2}} - 8D_{3\frac{1}{2}}$	1108.43	90218	10	-2		90217	4	-1
$7P_{1\frac{1}{2}} - 12D_{3\frac{1}{2}}$	2587.2	38640	0	0	$xxx\ h_0$	$6P_{1\frac{1}{2}} - 8D_{3\frac{1}{2}}$	1103.94	90585	10	3		90590	5d	-2
$6D_{1\frac{1}{2}} - 7F_{3\frac{1}{2}}$	2576.6	38799	8	-1	$x\ h_4$	$6P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	1065.58	93846	9	3				
$6D_{2\frac{1}{2}} - 7F_{3\frac{1}{2}}$	2526.7	39566	8	-1	$x\ h_3\ Z$	$6P_{1\frac{1}{2}} - 7D_{1\frac{1}{2}}$	1060.66	94281	10	3		94285	4	-1
$7P_{1\frac{1}{2}} - 13D_{3\frac{1}{2}}$	2521.1	39653	0	-5	h_0	$6P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$	1050.77	95168	10	8				
$7P_{1\frac{1}{2}} - 11D_{1\frac{1}{2}}$	2498.9	40005	2	2	h_0	$6P_{1\frac{1}{2}} - 9D_{3\frac{1}{2}}$	1049.82	95254	10	1				
$6D_{2\frac{1}{2}} - 10P_{1\frac{1}{2}}$	2445.1	40885	1	2		$6P_{1\frac{1}{2}} - 11S_{\frac{1}{2}}$		97489 (calc.)			k			
$6P_{1\frac{1}{2}} - 7F_{3\frac{1}{2}}$	2356.9	42414	1	0	$xx\ h_3$	$6P_{1\frac{1}{2}} - 10D_{1\frac{1}{2}}$	1016.61	98366	10		m			
$7P_{1\frac{1}{2}} - 13D_{1\frac{1}{2}}$	2355.3	42444	0	-4		$6P_{1\frac{1}{2}} - 12S_{\frac{1}{2}}$	1001.81	99819	6	12				
$6D_{2\frac{1}{2}} - 8F_{3\frac{1}{2}}$	2326.2	42976	1	0	$x\ h_2$	$6P_{1\frac{1}{2}} - 11D_{1\frac{1}{2}}$	995.89	100413	10		m			
$6D_{2\frac{1}{2}} - 11P_{1\frac{1}{2}}$	2280.8	43831	0	5		$6P_{1\frac{1}{2}} - 9S_{\frac{1}{2}}$	986.71	101347	10	-1	x			
$6P_{1\frac{1}{2}} - 7S_{\frac{1}{2}}$	2203.5	45368	2	-1	$x\ Z$	$6P_{1\frac{1}{2}} - 12D_{1\frac{1}{2}}$	982.17	101815	8		m			
From here on λ vac is given.						$6P_{1\frac{1}{2}} - 14S_{\frac{1}{2}}$	975.35	102527	1	7				
						$6P_{1\frac{1}{2}} - 13D_{1\frac{1}{2}}$	972.56	102823	9		$m\ H?$			
						$6P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	967.23	103388	10	6		103389	0	5
						$6P_{1\frac{1}{2}} - 14D_{1\frac{1}{2}}$	965.36	103588	3		m			
						$6P_{1\frac{1}{2}} - 15D_{1\frac{1}{2}}$	960.21	104144	2		m			
						$6P_{1\frac{1}{2}} - 8D_{1\frac{1}{2}}$	958.76	104301	2	-4				
						$6P_{1\frac{1}{2}} - 16D_{1\frac{1}{2}}$	955.91	104612	1		m			
						$6P_{1\frac{1}{2}} - 17D_{1\frac{1}{2}}$	952.92	104941	1		m			
						$6P_{1\frac{1}{2}} - 10S_{\frac{1}{2}}$	926.44	107940	5	-10				
						$6P_{1\frac{1}{2}} - 9D_{1\frac{1}{2}}$		109257 (calc.)			n			
						$6P_{1\frac{1}{2}} - 11S_{\frac{1}{2}}$	896.30	111570	3	4				
						$6P_{1\frac{1}{2}} - 10D_{1\frac{1}{2}}$	889.68	112400	8	9				
						$6P_{1\frac{1}{2}} - 12S_{\frac{1}{2}}$	877.96	113900	2	12				
						$6P_{1\frac{1}{2}} - 11D_{1\frac{1}{2}}$	873.71	114455	6	11				
						$6P_{1\frac{1}{2}} - 13S_{\frac{1}{2}}$	865.97	115477	1	19				
						$6P_{1\frac{1}{2}} - 12D_{1\frac{1}{2}}$	863.00	115875	3	10				
						$6P_{1\frac{1}{2}} - 13D_{1\frac{1}{2}}$	855.57	116681	3	18				
						$6P_{1\frac{1}{2}} - 14D_{1\frac{1}{2}}$	849.88	117664	2d	-14				
						$6P_{1\frac{1}{2}} - 15D_{1\frac{1}{2}}$	846.04	118198	2	25				
						$6P_{1\frac{1}{2}} - 16D_{1\frac{1}{2}}$	842.81	118651	1	17				
						$6P_{1\frac{1}{2}} - 17D_{1\frac{1}{2}}$	840.25	119012	00	12				

Notes and notation, Table I:

 $\Delta\nu = \nu_{\text{Predicted}} - \nu_{\text{Experimental}}$ x —line classified previously by Gieseler.⁹ xx —line classified by Gieseler, but with different assignment of the levels involved. xxx —line classified erroneously by Gieseler. h_0 —hyperfine structure observed by Rose; line single. $h_1, 2, \dots$ —hyperfine structure observed by Rose, similar to other lines marked $h_1, 2, \dots$ (a) This line may cover the line $sp^2\ ^2P_{\frac{1}{2}} - 9p\ ^2P_{\frac{1}{2}}$.

(b) This line may be covered by a Pb I line.

(c) The absence of hyperfine structure in this line is inconsistent with its previous classification by Gieseler as $sp^2\ ^4P_{\frac{1}{2}} - 7p\ ^2P_{1\frac{1}{2}}$, since the level from sp^2 would be expected to show structure.(d) Murakawa suggested on the basis of hyperfine structure that this line was a transition from $6s^2\ ^7p\ ^2P_{1\frac{1}{2}}$ to an unknown level with $J=2\frac{1}{2}$ which he called $6s6p^2\ ^4P_{2\frac{1}{2}}$; this level was located independently in the present work, and is differently assigned.

(e) This line was classified by Gieseler as Pb I; its hyperfine structure is definitely inconsistent with that classification, but agrees with the present one.

(f) This line may be covered by a Pb I line.

(g) Smith¹¹ classified a line at 4272.63A with intensity 5 as Pb III ($6s7s\ ^1S_0 - 6s7p\ ^1P_1$).(i) Smith¹¹ classified a line at 3689.32A, intensity 5, as Pb III ($6s7s\ ^3S_1 - 6s7p\ ^1P_1$).(j) This value of ν is questionable; however, Rose observed a line at this point which had the correct hyperfine structure for the transition here ascribed to it.(k) This line may be covered by a H line ($\lambda 1025.78$).

(m) Unresolved doublet.

(n) This line may be covered by a Hg line ($\lambda 915.83$).

made, with satisfactory general agreement. Comparison with the isoelectronic spectra Tl I and Bi III may be made by use of the regular and irregular doublet laws, as well as the similarity of relative positions of the sp^2 levels. The values of the screening constant s in the regular doublet law formula

$$\Delta\nu = f(I)(Z-s)^4/n^3$$

are given in Table III, where the agreement is as

satisfactory as could be expected for heavy atoms and in view of the existing perturbations. The agreement of the observed levels with the irregular doublet law is shown in Fig. 1. The principal deviations occur in differences involving the $6d\ ^2D$ terms, which are shown below to be considerably perturbed by neighboring sp^2 levels. In Fig. 2 the sp^2 levels of Pb II and Bi III are plotted together, with scales so adjusted that the separation of the extreme levels is equal. The

TABLE II. Term values and effective quantum numbers in Pb II—(Terms underlined are those previously found by Gieseler.⁹)

	$n=5$	6	7	8	9	10	11	12	13	14	15	16	17	18	19
$^2S_{1/2}$			61795 2.665	32063 3.700	19897 4.697	13313 5.742	9669 6.738	7331 7.738	5747 8.740	4628 9.739					
$^2P_{1/2}$		121243 1.903	46784 3.063	26166 4.096	16821 5.108	11743 6.114	8665 7.118	6658 8.120	5276 9.121	4285 10.121					
$\Delta\nu$		14081	2813	1161	598	351	222	150	105						
$^2P_{1/2}$		107162 2.024	43971 3.160	25005 4.190	16223 5.201	11392 6.207	8443 7.211	6508 8.213	5171 9.214						
$^2D_{1/2}$		51503 2.920	26959 4.035	17849 4.959	11986 6.051	8834 7.049	6777 8.048	5358 9.051	4344 10.052	3593 11.053	3020 12.056	2575 13.056	2221 14.057		
$\Delta\nu$		-776	1020	796	79	58	41	27	21	16	12	11	9		
$^2D_{2/2}$		52279 2.898	25939 4.114	17053 5.074	11907 6.072	8776 7.072	6736 8.073	5331 9.074	4323 10.077	3577 11.078	3008 12.080	2564 13.084	2212 14.087	1928 15.089	1695 16.092
$^2F_{2/2}$	28714 3.910	18362 4.890	12705 5.878	9297 6.871	7093 7.867	5586 8.864	4513 9.862	3721 10.86	3121 11.86						
$\Delta\nu$	-15	-13	-9	-6	-5	-4	-2	-2	-1						
$^2F_{3/2}$	28729 3.909	18375 4.888	12714 5.876	9303 6.869	7098 7.864	5590 8.862	4515 9.860	3723 10.858	3122 11.858	2655 12.858					
$^2G_{3/2, 4/2}$	17684 4.982	12275 5.980	9013 6.979	6897 7.978	5446 8.978	4410 9.98	3643 10.98	3060 11.98	2606 12.98	2247 13.98	1957 14.98				
	6s6p ²		$^4P_{1/2}$ $^4P_{3/2}$	63332 55119 47338		$^2D_{1/2}$ $^2D_{3/2}$	38160 32271		$^2P_{1/2}$ $^2P_{3/2}$	32995 16574		$^2S_{1/2}$	16946		

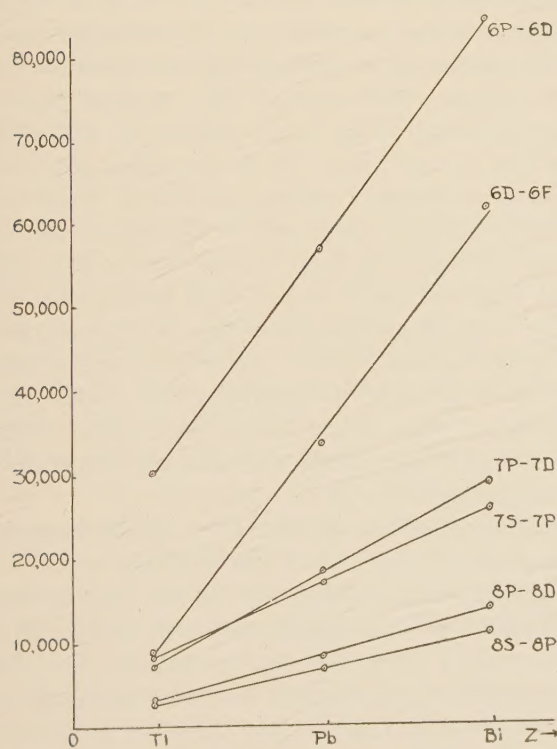
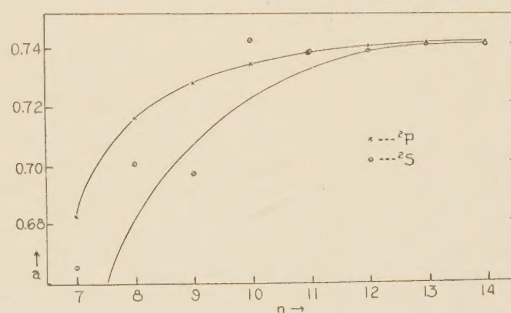


FIG. 1. Irregular doublet law.

FIG. 2. Irregularities in 2S series as shown by values of $a (\equiv n^* - m)$ vs. n .TABLE III. Regular doublet law. Values of s from $\Delta\nu = f(l)(Z-s)^4/n^3$.

	6P	7P	8P	9P	
Tl I	53.422	62.467	64.984	66.408	
	-3.443	-4.463	-4.253	-4.114	
Pb II	49.979	58.004	60.731	62.294	
	-2.278	-2.897	-2.739		
Bi III	47.701	55.107	57.992		
	6D	7D	8D	9D	10D
Tl I		70.262	70.852	71.255	71.470
Pb II	(inverted)	56.587	56.511	66.341	66.367
Bi III		60.615	62.025		

general agreement is evident; particular deviations are discussed below as due to perturbations.

SUBSTANTIATIONS AND PERTURBATIONS

The Zeeman pattern observations by Green and Loring¹⁵ were used to check the present classification. A recalculation from the observed patterns was necessary, since the present classification changes Gieseler's assignment of several levels and includes several lines which were unclassified when their patterns were observed. Table IV is a revision of Table III of reference 15,

TABLE IV. *g*-values for even levels of Pb II.

λ	$7S_{\frac{1}{2}}$	$4P_{\frac{1}{2}}$	$6D_{\frac{3}{2}}$	$6D_{\frac{1}{2}}$	$4P_{\frac{3}{2}}$	$7D_{\frac{1}{2}}$	$7D_{\frac{3}{2}}$	$9S_{\frac{1}{2}}$	$8D_{\frac{1}{2}}$	$8D_{\frac{3}{2}}$
2203	2.02									
2719*		0.55								
2948			1.29							
3016				0.89						
3452					1.41					
3455									1.07	
3714										1.16
3718								1.93		
3786		1.65								
3827										
									(.51 fr σ .92 fr π)	
4153								1.98		
4242			1.29							
4245			1.35							
4386				.86						
5042						0.81				
5372					1.67					
5545							1.18			
5609	2.00									
5876						.78				
6660	2.02									
Ave.	2.01	1.65	1.31	.87	1.54	.80	1.18	1.96	.99	1.16
Theor.	2.00	1.73	1.20	.80	1.60	.80	1.20	2.00	.80	1.20

* There appears to be a confusion between $\lambda 2719.8$ and $\lambda 2717.5$. Green and Loring remark that $\lambda 2717.5$ appears to have a pattern similar to $\lambda 3786$, thus appropriate to the $6F_{\frac{3}{2}} - sp^2 4P_{\frac{1}{2}}$ transition to which $\lambda 2719.8$ is assigned. (This assignment is required by the frequency difference in the two levels and by the hyperfine structure of $\lambda 2719.8$.) However, the Zeeman pattern given by them for $\lambda 2719$ leads to inconsistent results for the *g*-value of $7S_{\frac{1}{2}}$ if attributed to $\lambda 2717.5$.

and gives the *g*-values for the various even levels, calculated from the unresolved patterns by the method of Shenstone and Blair,¹⁶ assuming in each line that the odd level involved has the appropriate theoretical (i.e., unperturbed) *g*-value. Comparison with the theoretical *g*-values for the even levels shows good agreement. The effect of the mutual perturbation between the two levels $sp^2 4P_{\frac{1}{2}}$ and $6d^2 D_{\frac{1}{2}}$, and between $6d^2 D_{\frac{3}{2}}$ and $sp^2 4P_{\frac{3}{2}}$, is shown by the

tendency to share *g*-values, thus decreasing the *g*-values of the sp^2 levels approximately as much as the $6d$ level values are increased. Further evidences of these perturbations exist in the hyperfine structure of the levels, and in their positions, as discussed below.

Hyperfine structure data made available by Dr. J. L. Rose were used as a guide to assigning the sp^2 levels and as a further indication of perturbations existing between various even levels. Levels from sp^2 should show a larger separation in the components of the Pb 207 isotope (due principally to the increased interaction of the single *s* electron with the nucleus); and the isotope shift for Pb 206 and 208 should be different for the sp^2 levels as compared with the normal s^2x levels. Inspection of the data in Dr. Rose's article immediately following shows that the sp^2 levels as assigned do have consistently larger hyperfine structure separations. These separations also substantiate the perturbations expected between such even terms as have equal *J*-values and are located in proximity to each other. Such perturbations would cause a sharing of the larger separations of the sp^2 levels with those from the normal s^2s and s^2d configurations. This sharing is shown by the fact that the sum of the isotope shifts for $sp^2 4P_{\frac{1}{2}}$ and $6d^2 D_{\frac{1}{2}}$ is approximately equal to the sum of the shifts for $sp^2 4P_{\frac{3}{2}}$ and $6d^2 D_{\frac{3}{2}}$. A similar effect on the hyperfine structure appears in the $8d^2 D$ terms. Since $7d^2 D_{\frac{1}{2}}$ is single and $7d^2 D_{\frac{3}{2}}$ shows only a small structure (perhaps due to interaction with $sp^2 2D_{\frac{3}{2}}$), the $8d^2 D$ terms would be expected to show vanishingly small structure. The separation observed in the $8d^2 D_{\frac{1}{2}}$ level is thus due to the effect of the neighboring level $sp^2 2P_{\frac{1}{2}}$, while the absence of such separation in the $8d^2 D_{\frac{3}{2}}$ level is in complete agreement with the absence of any neighboring term with $J=2\frac{1}{2}$.

Since the odd terms in the Pb II spectrum include only the $2P$ and $2F$ series from $6s^2mx$, no perturbations should occur, on account of the inequality of *J*-values for adjacent levels. This absence of perturbations is evident in the regularity of the effective quantum numbers of these series in Table II. On the other hand, the even terms show a mixing of the levels from sp^2 with the $6s^2ms$ and $6s^2md$ configurations. The

¹⁵ Green and Loring, Phys. Rev. 43, 459 (1933).

¹⁶ Shenstone and Blair, Phil. Mag. 8, 765 (1929).

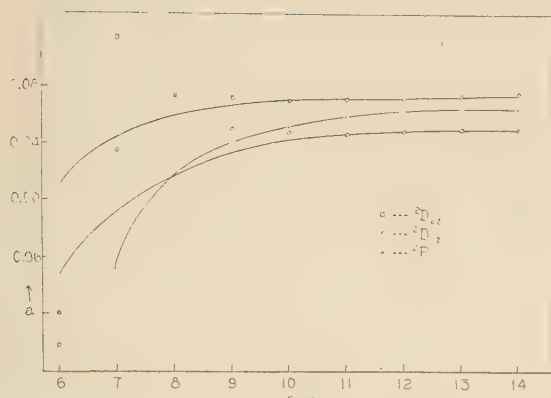


FIG. 3. Irregularities in 2D series as shown by values of a ($\equiv n^* - m$) vs. n .

resulting mutual perturbations are particularly evident in the locations of the series members, and may be explained very satisfactorily, though qualitatively, by the concepts of Langer¹⁷ and Shenstone and Russell.¹⁸ They find that the perturbation between two interacting levels is a mutual repulsion whose magnitude depends on the overlapping of the wave functions of the two levels, and hence should increase with increasing proximity of the levels. If the quantum number discrepancy a of the Rydberg series formula be plotted against the total quantum number n (Fig. 2), the higher $6s^2ms$ series members are evidently regular; at $n=11$ and 10 an increasing deviation is apparent, due to repulsion by the $sp^2 {}^2S_{1/2}$ level; at $n=9$ the effect of this perturbation is reversed in direction, causing the value of a to be smaller than normal. The value of a for the $8s$ term is too large, agreeing with the expected effect of the neighboring $sp^2 {}^2P_{1/2}$ level. And finally, the $7s$ value of a is also too large, due to the effect of $sp^2 {}^4P_{1/2}$.

Similarly explainable effects are found in the case of the 2D series, for which the effective quantum number discrepancy is plotted against n in Fig. 3. Again the higher members are regular, but in the ${}^2D_{11/2}$ terms at $n=10$ and 9 there appears a deviation due to the presence of the $sp^2 {}^2P_{11/2}$ level. This in turn causes a reversed effect upon $8d {}^2D_{11/2}$, decreasing the effective quantum number below its normal value. The $7d {}^2D_{11/2}$ level is

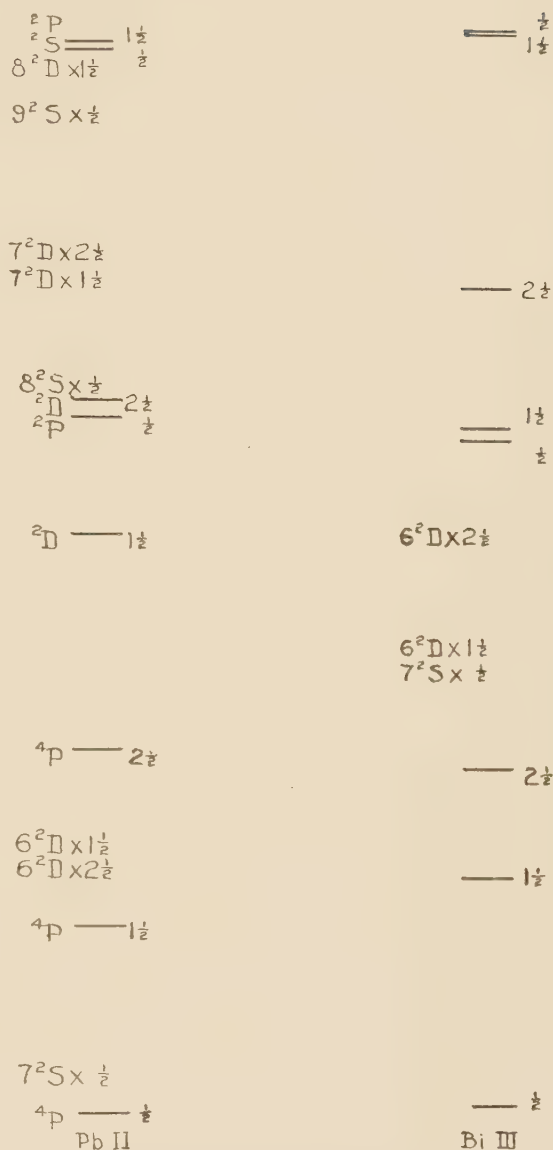


FIG. 4. sp^2 levels from Pb II and Bi III. (The α 's indicate the location of terms of the normal (s^2nx) series.)

affected by both $sp^2 {}^2P_{11/2}$ and $sp^2 {}^2D_{11/2}$, so a prediction of the net effect is not immediately possible; this is also true of the $6d {}^2D_{11/2}$, affected by $sp^2 {}^2D_{11/2}$ and $sp^2 {}^4P_{11/2}$. In the case of the ${}^2D_{21/2}$ series the deviations of the terms $n=10, 9, 8$ and 7 are due to repulsion by the $sp^2 {}^2D_{21/2}$ level; the relative magnitudes and directions of these displacements are in accord with expectation. Further, the $6d {}^2D_{21/2}$ term is displaced in the direction of smaller effective quantum number

¹⁷ Langer, Phys. Rev. 35, 649 (1930).

¹⁸ Shenstone and Russell, Phys. Rev. 39, 415 (1932).

by the proximity of $sp^2\ ^4P_{2\frac{1}{2}}$. These perturbation effects explain very satisfactorily the inversion of the $6d\ ^2D$ and the abnormally large separations of the $7d$ and $8d$ doublets as observed.

The effect of the perturbations on the sp^2 levels is not so readily discussed, since the unperturbed arrangement is not so well known. Referring to Fig. 4, however, the larger separation of the $^4P_{1\frac{1}{2}}-^4P_{2\frac{1}{2}}$ levels in Pb II may well be due to the presence of the $6d\ ^2D$ terms, both of which would tend to increase the separation. In Bi III¹⁹ the

¹⁹ McLay and Crawford, Proc. Roy. Soc. A143, 540 (1934).

effect does not occur, since the $6d$ doublet lies above the 4P group. The difference in location of the $sp^2\ ^2D_{2\frac{1}{2}}$ levels in the two spectra may be explained by the downward effect of the $7d\ ^2D_{2\frac{1}{2}}$ term in Pb II and the upward effect of $6d\ ^2D_{2\frac{1}{2}}$ in Bi III. The perturbations existing in the sp^2 levels with $J=\frac{1}{2}$ and $1\frac{1}{2}$ appear too complicated to admit of present interpretation on a qualitative basis.

The friendly cooperation of Dr. Rose by the loan of plates and the communication of unpublished hyperfine structure data is gladly acknowledged.

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